

Topical Report

COMBINATION ALKALINE-SURFACTANT FLOODING: A STATE-OF-THE-ART REVIEW

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ABSTRACT

A review is presented of recent laboratory work reported in the literature on enhanced oil recovery by combination alkaline-surfactant flooding. Consideration is given to surface activity, adsorption, and interaction with divalent cations, along with oil recovery in corefloods. The topics examined are low-acid oils, systematic optimization, ion specificity, mixed alkalis, and injection strategies. It is concluded that alkali-surfactant flooding shows much promise of being cost effective. Areas for further research are indicated.

INTRODUCTION

This report presents part of NIPER's program on novel EOR methods, and specifically addresses the emerging technique of mobilizing oil by injection a combination of alkaline and surfactant chemicals in low concentrations. The report is based on work performed for the Department of Energy under Project BE14, Task 1, and constitutes a status report as specified in Milestone 5.

The combination of surfactant and alkaline agents for recovery of oil has been advocated in various forms for more than 30 years. The observation of a synergy¹⁻⁵ has been explained by a variety of mechanisms. The enhancement of interfacial tension (IFT) reduction may be due to improved hydrophilic-lyophilic balance (HLB) when preformed surfactants supplement saponified petroleum acids.⁶ Moreover, the adverse effects of divalent cations (in the brine or on exchange sites) on IFT may be reduced by precipitation or sequestering.^{3,7} Surfactants and alkaline agents are both claimed to fluidize rigid films at the oil-brine interface,^{1,8} which facilitates coalescence of oil ganglia. The alkalis increase the effectiveness of surfactants (and also polymers) by reducing their adsorption substantially.^{7,9-13} The ability of alkalis to alter wettability^{11,14-15} can improve recovery by surfactants or degrade it. In some cases, alkalinity improves sweep efficiency by precipitation or wettability alteration,^{16,17} or emulsification.¹⁸ Several strategies have been devised:

1. (SA)P: the combination of alkali and surfactant into a single slug, usually followed by polymer.^{1-7,11,16-17,19}
2. A(SA)P: preinjection of alkali to condition the reservoir followed by a surfactant-alkali combination and then polymer.^{9-10,13-14,19}
3. S(AP): a surfactant slug followed by alkaline polymer.¹⁸
4. Injection of oil-soluble acids, followed by water-soluble alkalis.²⁰⁻²³
5. A gradient in surfactant concentration²⁴, or ancillary gradients in salinity.^{17,18}

A review of the recent literature indicates several areas of research that can lead to better understanding and improved design of alkaline-surfactant flooding systems.

RECOMMENDED AREAS OF RESEARCH

Application to Low-Acid Oils

The efficiency of alkaline flooding for oil recovery is assumed to be contingent on the presence of petroleum acids occurring naturally in the oil. Their effect depends on the properties of the anion, which can vary from acid to acid. Thus, a screening criterion such as "acid number greater than 0.1" is of only limited usefulness.²⁵⁻²⁶ Martin, Oxley, and Lim²⁷ and Krumrine, Falcone, and Campbell¹⁹ have presented promising results when the combination of alkali and surfactant is used with oils at or below this limit. In both cases, alkali alone achieved a very limited reduction of IFT (down to about 1 dyne/cm), and gave no tertiary oil recovery. However, Martin et al.,²⁷ whose oil had an acid number 0.05, found a very significant reduction of IFT when alkali was added to surfactant, as shown in figure 1. It should be emphasized that the comparison was made between the minima in the IFT curves, and is not simply a shift in optimal salinity. It is not clear from the data whether any of the effect was due to hardness suppression.

Figures 2, 3, and 4 show some interesting results obtained by Krumrine et al.¹⁹ Comparison of figures 2 and 3 shows that the IFT response to surfactant plus alkali is oil-specific. Either the alkali reacts significantly even with

a low-acid oil, or it reacts with the surfactant in such a way as to alter its solubility in the particular oil. Similarly, figures 3 and 4 show that the alkali effect is surfactant-specific with the same oil, apart from any divalent-ion or adsorption effects. Results reported in another paper,²⁸ from the same laboratory, show that silicate reduced the IFT in soft brine, but did not enhance the effect of the surfactant. (Contrary to a statement in the conclusions of the paper, silicate did not increase tolerance to hardness.) Research that leads to better understanding of these effects will contribute to improved design of (SA)P floods. The importance of such a program is illustrated by further data from reference 19. Table 1 shows the improvement in coreflood recovery of the low-acid oil when alkalis were added to surfactant, all other things being unchanged. Extending the comparison to lowering of IFT and adsorption reduction, the increasing order of effectiveness is as follows:

Recovery: none \approx NaOH $<$ Na_3PO_4 \approx Na_2CO_3 $<$ $\text{Na}_5\text{P}_3\text{O}_{10}$ $<$ silicate $<$ (silicate + Na_2CO_3)

IFT lowering: none $<$ $\text{Na}_5\text{P}_3\text{O}_{10}$ $<$ silicate $<$ Na_2CO_3 $<$ NaOH

Adsorption reduction: none $<$ NaOH $<$ Na_2CO_3 $<$ Na_3PO_4 $<$ $\text{Na}_5\text{P}_3\text{O}_{10}$ $<$ silicate

TABLE 1. - Coreflood recoveries of oil (acid number 0.10^1)
by surfactant² with various alkaline agents

Alkali	Residual oil recovery, %
None	34.9
0.367 % Na_2CO_3	51.0
0.367 % silicate ⁴	60.5
0.367 % $\text{Na}_5\text{P}_3\text{O}_{10}$	62.0
0.5 % silicate + 0.185 % Na_2CO_3	59.5

¹mgKOH/g oil.

²Petrostep 450.

³From table 3 of reference 19: 0.25 PV preflush of 1 % NaCl; 3.0 PV of 0.25 % PS450 in 1.0 % NaCl, with alkali as indicated.

⁴ $\text{SiO}_2/\text{Na}_2\text{O} = 3.2/1$

This shows that the benefit of alkali to recovery is more closely correlated with adsorption reduction than with IFT lowering. The silicate in these experiments had a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 3.2. Specific recommendations for further research are:

1. Controlled variation of petroleum acids. Observe surface activity of added surfactant, alkali, and their combination, with mixtures containing increasing amounts of petroleum acids, starting from a baseline of refined oil. Different chemical types of petroleum acids should be used.
2. Test the effect of increasing hardness, which may be distinct from interfacial activity. The various hardness cations are likely to have individual effects.
3. Develop further data on reduction of surfactant adsorption by alkalis, which is indicated to be the major benefit with low-acid oils.

Systematic Optimization

The benefit of adding alkali to a surfactant can be measured either as increased recovery or reduced chemical requirements.¹⁸⁻¹⁹ The latter is illustrated in table 2. In many cases, the benefit stems from improved sweep efficiency or reduced adsorption.^{13,16-17} The converse improvement on adding surfactant to alkali can be attributed to interfacial effects.⁶ With low-acid oils, the effect of surfactant on alkali is more pronounced than the effect of alkali on surfactant.^{19,27} For optimization, the mixture must therefore be tailored to each oil and reservoir.

Figures 4 and 5 illustrate that the first addition of either alkali or surfactant has a larger effect on IFT than subsequent increases in concentration. Interfacial activity is a function of pH, salinity, and surfactant species. Salinity requirement diagrams, such as figures 6, 7, 8, and 9, provide a means for designing chemical slugs with the maximum interfacial activity. The dotted lines in figure 8 suggest the design of a A(SA)P flood: an alkaline preflush at 3 % NaCl, followed by a slug with 1 % surfactant blend at 0.5 % NaCl. This should traverse the region of low IFT with a minimum amount of surfactant. The mobility slug at 2 % NaCl will stay

in the lower-phase microemulsion region, conforming with the principle of the salinity gradient,²⁹ but remaining in the region of alkaline low IFT (fig. 7). Schuler et al.¹⁸ carried out a laboratory coreflood experiment on the system of figure 8, but without an alkaline preflush, and with 2 % NaCl in the surfactant slug. This would be traced in the beginning by the dotted line in figure 6, but the phase diagram would be changing to that in figure 8. The alkali in the surfactant slug increased tertiary recovery by a factor of 2.5 over that recovered with surfactant alone (other things being equal). It would be interesting to compare recovery when an alkaline preflush was used, as suggested by figure 8. With fairly acid oils, for which interfacial effects dominate, the phase and IFT behavior should be mapped in extended "salinity requirement diagrams" as a function of surfactant concentration, alkali concentration, and salinity. The results should be used as a first step in determining optimum composition of chemical slugs.

TABLE 2. - Comparison of chemical recoveries. (Alkali is sodium hydroxide and polymer is polyacrylamide.)

Investigators	Flood type			
	P	SP	AP	SAP
<u>Schuler et al. (ref. 18)¹</u>				
surfactant ²		0.30		0.10
alkali ²			0.75	0.75
polymer ³		2500	2000	3000
tertiary recovery, %		83	61	83
<u>Lin et al. (ref. 30)⁴</u>				
surfactant ²				0.031
alkali ²			0.28	0.25
polymer ⁵	0.86		0.80	0.54
tertiary recovery, %	31		46	73

¹ California oil, 27° API, acid number 0.5 mg KOH/g oil; surfactant is a proprietary sulfonate blended with an ethoxylated alcohol.

² Amount injected, concentration (%) X PV.

³ Amount injected, concentration (ppm) X PV.

⁴ 26° API oil from Grand Forks, Alberta Petroleum sulfonate surfactant.

⁵ PV injected (concentration not specified in reference).

Figures 7 and 8 emphasize the above conclusions that both alkali and surfactant have a threshold concentration for the achievement of low IFT, and that concentrations above the threshold have little additional benefit. However, figures 9 and 10 indicate that the phenomena are more complex. In some saturation regions, the optimal salinity continues to increase with added surfactant, as in the absence of alkali (fig. 6). The behavior may depend on the HLB relation between added and generated surfactants. This is another area in which investigations leading to better understanding would contribute to improved process design.

Comparison of figures 6 and 8 also illustrate that the salinity width of the optimal region is increased by adding alkali to the surfactant. This should be reflected by an increased tolerance to salinity variations.

Low-pH Alkaline Agents

Current work at NIPER is focused on the use of sodium bicarbonate or its mixtures with sodium carbonate.³¹ It is essential to combine this with surfactant, because at the low pH attained the alkali itself does not generate much interfacial activity or mobilize oil very well. However, the alkali-surfactant combination usually performs better than the surfactant alone. This is partly due to adsorption and divalent ion effects, as in the case of low-acid oils, and partly due to emulsification effects.³²

Ion Specificity

The work of Krumrine et al.¹⁹ (fig. 11) indicates that the interfacial effects of alkaline agents are primarily a pH effect. This appears to be supported in figure 1 from the data of Martin et al.²⁷ On the other hand, the latter authors present a pH scan that minimizes specific ion effects by interchanging only OH^- for Cl^- and H^+ for Na^+ . The result of these measurements was that IFT was not altered from pH 5.5 to 12. However, there is an order of magnitude discrepancy with other results in the same paper, in addition to the conflict with figure 11. In more recent work from Krumrine's laboratory, shown in figure 12,¹⁷ emulsion phase behavior suggests that pH and anion species are independently important; however, the authors use crude-oil acidity, pH, and conductivity to calculate that the optimum condition for all three systems is pH 11.5 and conductivity 4.7 reciprocal ohm-meters. In

table 3, data of Lin, Besserer, and Pitts³⁰ show a difference between sodium hydroxide and sodium orthosilicate at similar values of pH. The difference is reversed and augmented in the presence of a surfactant. Table 1 also implies specific anion effects. It is evident that our knowledge of the specific effects of anions and the relative role of pH, has not been well formulated. This is an area that needs further work to develop an understanding of the factors that affect performance. One approach would be to run a scan of compositions between two different alkalis, while monitoring changes of pH and ionic strength.

It is of academic interest to note that figure 1 shows an effect of the cation on IFT, and the effect on the optimal salinity in figure 13 is even more striking. In the latter case the anion seems to make little difference.

Krumrine and Falcone²⁸ present data showing that individual ions also affect polymer viscosity in different ways. The results in figure 14 are counterintuitive as far as ionic strength is concerned. The conductivities of table 4 are used to estimate the ionic strengths: 0.36 eq/L for sodium carbonate, 0.42 eq/L for sodium hydroxide, and 0.53 eq/L for sodium orthosilicate. Speculations that account in part for the results in figure 14 are:

1. Sodium hydroxide is least efficient in counteracting hardness.
2. Sodium carbonate is least efficient in hydrolyzing the polyacrylamide.
3. Sodium orthosilicate has a significant viscosity of its own.

These speculations need to be supported by experimental evidence.

TABLE 3. - Effect of alkalis on IFT of Grand Forks oil¹

	Interfacial tensions, dyne/cm	
	No surfactant	0.3 % petroleum sulfonate
No alkali	11.2	5.3
0.8 % NaOH pH \approx 13.3	2.1	0.003
0.8 % Na ₄ SiO ₄ (pH \approx 13.0)	1.4	0.046

¹From reference 30. Brine contains 40 ppm Ca + Mg

Mixed Alkalies

Values of pH for the maximum in buffer capacity for different alkalis are given in table 5. If some intermediate value is preferable for a particular reservoir because of mineralogy and/or oil acidity, this could be tailored by using mixtures.

TABLE 4. -Comparison of alkalis¹

	Total alkali, ² %	Active alkali ³ fraction	pH	Conductivity reciprocal ohm-meters (1 % solution)	Primary anion ⁴
NaOH	77.5	0.98	13.3	4.86	OH ⁻
Na ₄ SiO ₄	67.4	0.91	13.0	2.94	SiO ₃ ⁼
Na ₂ SiO ₃	50.8	0.88	12.5	1.92	SiO ₃ ⁼
Na ₂ CO ₃	58.5	0.21	11.3	1.31	CO ₃ ⁼
Na ₃ PO ₄	62.8	0.30	11.81	1.41	HPO ₄ ⁼

¹From table 1 of reference 17.

²Percent Na₂O.

³Fraction of total alkali neutralized by titration to pH 10.

⁴Based on pH and conductivity.

TABLE 5. - Buffer points for the common alkalis at 25° C

Anion	pH
Orthosilicate ¹	9.7, 11.7, 12.0
Metasilicate ¹	9.7, 12.0
Carbonate ¹	10.2
Orthophosphate ¹	7.2, 12.7
Tripolyphosphate ²	8.0

¹From Handbook of Chemistry and Physics (Chemical Rubber Publishing Co.).

²From reference 33.

Each alkali has its own capacity for reducing divalent cations. Because of solubility considerations, carbonate is efficient at precipitating calcium, while hydroxide and silicate are superior for precipitating magnesium. Phosphate, depending on the pH, can remove calcium, by a combination of precipitation and complexing, more completely than can carbonate.³¹ It complexes magnesium slightly more than calcium.³⁴ For divalent ion control, a mixture of alkalis could be expected to perform better than any one alone. Krumrine and Falcone¹⁷ found that a 4:1 mixture of silicate and carbonate produced as much precipitate as silicate alone, but with the mixture the precipitate was less flocculant and gave less plugging. Krumrine, Falcone, and Campbell¹⁹ reported that silicate was the best alkali for reducing surfactant adsorption, but was itself consumed the most. Carbonate was transmitted with little loss, and although it did not eliminate surfactant retention, it allowed the release of much of the surfactant in the post-flush (fig. 15), perhaps because of salinity gradient effects. It is plausible that a mixture of carbonate and silicate could buffer at a low enough pH to avoid mineral consumption reactions, but retain the capability of reducing adsorption. Extending research in this field to the use of mixed alkalis, blended to take advantage of individual capabilities, would probably lead to significant advances in the technology.

Injection Strategies

An alkaline preflush^{9-10,13-14,19} is intended to precondition a reservoir and make a subsequent surfactant process more effective. In one case (reference 19, tests 164 and 165), when a test with an alkaline preflush was compared with a neutral preflush followed by a surfactant + alkali, the alkaline preflush resulted in higher recovery. On the other hand, Schuler¹⁸ claimed that leading with a surfactant slug and following with an alkaline polymer gave broader valleys of low IFT (table 6), and a desirable low-mobility region behind the surfactant slug (fig. 16), presumably due to emulsification. Identification of the best injection strategy is an aspect of optimization that needs to be addressed by coreflood tests. Such investigations should also test the efficiency of reducing chemical demand by tapering of the surfactant, alkaline, and polymer concentrations. The performance will probably be dependent on rock type.

TABLE 6. - Interfacial activity of effluents in coreflood tests¹

Oil acid no. gKOH/g oil	Chemical strategy	Minimum IFT mdyne/cm	² PV to mdyne/cm	³ PV at mdyne/cm
0.5	SP	5	0.08	0.9
1.4	SP	"a few"		1.0
0.5	AP	20		1.5
1.4	AP	5	0.22	1.0
0.5	⁴ S (AP)	3	0.43	1.1
1.4	⁴ S (AP)	3	0.42	0.8

¹From reference 19.

²Amount of fluid injected before IFT fell to 10 μ N/m.

³Injection interval in PV over which IFT < 10 μ N/m.

⁴0.1 PV surfactant + polymer followed by 1.0 PV alkali + polymer.

As a matter of related interest, Krumrine and Falcone²⁸ found that the combination of alkali and polymer was more effective when the two chemicals were injected simultaneously than when injected successively in either order. The polymer improves the sweep efficiency of the alkali, and the alkali protects the polymer and maintains its viscosity.

In view of the numerous parameters to be investigated, a research program in this area should be constructed with the aid of numerical modeling, and factorial design should be used to determine trends.

CONCLUSIONS

Flooding using combinations of surfactant and alkali is emerging as an advancement over the use of either surfactant or alkali alone. Several mechanisms are involved that are partly understood, such as surface activity, adsorption, hardness suppression, and mobility control. The interplay among these factors will be specific for each oil and reservoir, and must be balanced out in optimizing the process. "Salinity requirement diagrams" will be of value. Two types of such scans are desirable: surfactant-salinity and surfactant-alkalinity. This will aid in minimizing chemical requirements.

Not well understood are specific effects of individual cations and anions. Systematic research on mixed alkalis is recommended for tailoring optimal pH, buffer capacity, sequestering, and adsorption. Most of the physicochemical effects are dynamic, and their role can be fully appraised only in coreflood tests. Various injection strategies are possible -- alkali first, surfactant first, concentration gradients, etc. -- and each has its own theoretical advantages. An extended experimental investigation of their relative merits would contribute much to improving the process.

It would be important to determine whether there are "windows" for the various effects, so that the ranges to be studied will have significance.

REFERENCES

1. Reisberg, J., and T. M. Doscher. Interfacial Phenomena in Crude Oil - Water Systems. Producers Monthly, November 1956, pp. 43-50.
2. Krehbiel, D. D., M. D. Gregory, C. R. Clark, and C. D. Kennedy. Method of Using Overbased Sulfonate Waterflood Additive Derived from Heavy Coker Gas Oil. U.S. Patent 3,804,170, Apr. 16, 1974.
3. Gale, W. W. and E. I. Sandvik. Tertiary Surfactant Flooding: Petroleum Sulfonate Composition Efficacy Studies. Soc. Pet. Eng. J., August 1973, pp. 191-199.
4. Chiu, Y. C. Tall Oil Pitch in Chemical Recovery. Soc. Pet. Eng. J., December 1980. pp. 439-449.
5. Radke, C. J. Additives for Alkaline Recovery of Heavy Oil. Proc. 1982 Ann. Heavy Oil/EOR Contractor Reports, July 27-29, 1982. U.S. Department of Energy CONF-820712.
6. Nelson, R. C., J. B. Lawson, D. R. Thigpen, and G. L. Stegemeier. Cosurfactant-Enhanced Alkaline Flooding. Pres. at the Fourth SPE/DOE Symp. on Enhanced Oil Recovery, Tulsa, OK, Apr. 15-18, 1984. SPE/DOE paper 12672.
7. Hill, H. J., J. Reisberg, and G. L. Stegemeier. Aqueous Surfactant Systems for Oil Recovery. J. Pet. Tech., February 1973, pp. 188-194.
8. Strassner, J. E. Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions. J. Pet. Tech., March 1968, pp. 303-312.
9. Feuerbacher, D. G., and M. K. Hrncir-Smith. Oil Recovery Process. U.S. Patent 3,777,817, Dec. 11, 1973.

10. Burdyn, R. F., H. L. Chang, and E. L. Cook. Oil Recovery by Alkaline/Surfactant Waterflooding. U.S. Patent 4,004,638, Jan. 25, 1977.
11. Dunlap-Wilson, P. M., and C. F. Bradner. Aqueous Surfactant Solutions Which Exhibit Ultra-low Tensions at the Oil/Water Interface. J. Coll. & Interface Sci., July 1977, pp. 473-479.
12. Somasundaran, P. and H. S. Hanna. Adsorption of Sulfonates on Reservoir Rocks. Pres. at the Fifth SPE Symp. on Improved Methods for Oil Recovery, Tulsa, OK, Apr. 16-19, 1978, SPE paper 7059.
13. Holm, L. W. and S. D. Robertson. Improved Micellar/Polymer Flooding with High pH Chemicals. J. Pet. Tech., January 1981, pp. 161-172.
14. Needham, R. B., G. R. Glinsman, and D. R. Wier. Oil Recovery by Improved Surfactant Flooding. U.S. Patent 4,004, 637, Jan. 25, 1977.
15. Kondrashev, O. F., A. G. Knyshenko, B. M. Leibert, and I. L. Markhasin. Effect of the Solid Phase of a Formation on the Mechanism of Oil Displacement by Surfactant and Alkali Solutions. Neft. Khoz., No. 7, July 1984, pp. 46-48. [Petroleum Abstracts No. 395,042].
16. Krumrine, P. H., J. S. Falcone, Jr., and T. C. Campbell. Surfactant Flooding II: The Effect of Alkaline Additives on Permeability and Sweep Efficiency. Soc. Pet. Eng. J., December 1982, pp. 983-992.
17. Krumrine, P. H. and J. S. Falcone, Jr. Beyond Alkaline Flooding: Design of Complete Chemical Systems. Pres. at the SPE Int'l Symp. on Oilfield Chemistry, San Antonio, TX, Feb. 4-6, 1987. SPE paper 16280.
18. Schuler, P. J., R. M. Lerner, and D. L. Kuehne. Improving Chemical Flood Efficiency with Micellar/Alkaline/Polymer Processes. Pres. at the Fifth SPE/DOE Symp. on Enhanced Oil Recovery, Tulsa, OK, Apr. 20-23, 1986. SPE/DOE paper 14934.
19. Krumrine, P. H., J. S. Falcone, Jr., and T. C. Campbell. Surfactant Flooding I: The Effect of Alkaline Additives on IFT, Surfactant Adsorption, and Recovery Efficiency. Soc. Pet. Eng. J., August 1982, pp. 503-513.
20. Reisberg, J. Secondary Recovery Method. U.S. Patent 3,174,542, Mar. 23, 1965.
21. Bernard, G. G. and O. C. Holbrook. Recovery of Oil From Subterranean Formations. U.S. Patent 3,185,214, May 25, 1965.
22. McCardell, W. M. Method of Secondary Recovery Using Surfactants Formed In Situ. U.S. Patent 3,298,436., Jan. 17, 1967.

23. Reisberg, J. Secondary Recovery Method. U.S. Patent 3,330,344. July 11, 1967.
24. Lawson, J. B. and D. R. Thigpen. Staged Preformed-Surfactant-Optimized Aqueous Alkaline Flood. U.S. Patent 4,502,541. Mar. 5, 1985.
25. Mayer, E. H., R. L. Berg, J. D. Carmichael, and R. M. Weinbrandt. Alkaline Injection for Enhanced Oil Recovery - A Status Report. J. Pet. Tech., January 1983, pp. 209-221.
26. Ball, J. T. Mechanisms of Alkaline Flooding. Sect. 13 in Chemical EOR: Searching for the Right Solution, Denver, CO, May 13-14, 1985. Pasha Publications, Arlington, VA.
27. Martin, F. D., J. C. Oxley, and H. Lim. Enhanced Recovery of a "J" Sand Crude Oil with a Combination of Surfactant and Alkaline Chemicals. Pres. at the SPE 60th Ann. Tech. Conf., Las Vegas, NV, Sept. 22-25, 1985. SPE paper 14293.
28. Krumrine, P. H. and J. S. Falcone, Jr. Surfactant, Polymer, and Alkali Interactions in Chemical Flooding Processes. Pres. at the SPE Int'l Symp. on Oilfield and Geothermal Chemistry, Denver, CO, June 1-3, 1983. SPE paper 11778.
29. Hirasaki, G. J., H. R. van Domselaar and R. C. Nelson. Evaluation of the Salinity Gradient Concept in Surfactant Flooding. Soc. Pet. Engineers J., June 1983, pp. 486-500.
30. Lin, F. F. J., G. J. Besserer, and M. J. Pitts. Laboratory Evaluation of Crosslinked Polymer and Alkaline-Polymer-Surfactant Flood. J. Canadian Pet. Tech., November-December 1987, pp. 54-65.
31. Peru, D. A. and P. B. Lorenz. Surfactant-Enhanced Low pH Alkaline Flooding. NIPER Paper No. EPR/OP-88/8. Submitted to J. Petrol. Technol. (April 1988).
32. Peru, D. A. and P. B. Lorenz. The Effect of Equilibration Time and Temperature on Drop-Drop Coalescence Time of Wilmington Crude Oil in a Weakly Alkaline Brine. NIPER Report No. EPR/OP-87/25. Accepted for publication in Chemical Engineering Communications, (July 1988).
33. Butler, J. N. Ionic Equilibrium. Adison-Wesley Publishing Co., Inc., 1964.
34. Van Wazer, J. R. Phosphorous and Its Compounds, v. I Chemistry. Interscience Publishers, Inc., 1958.

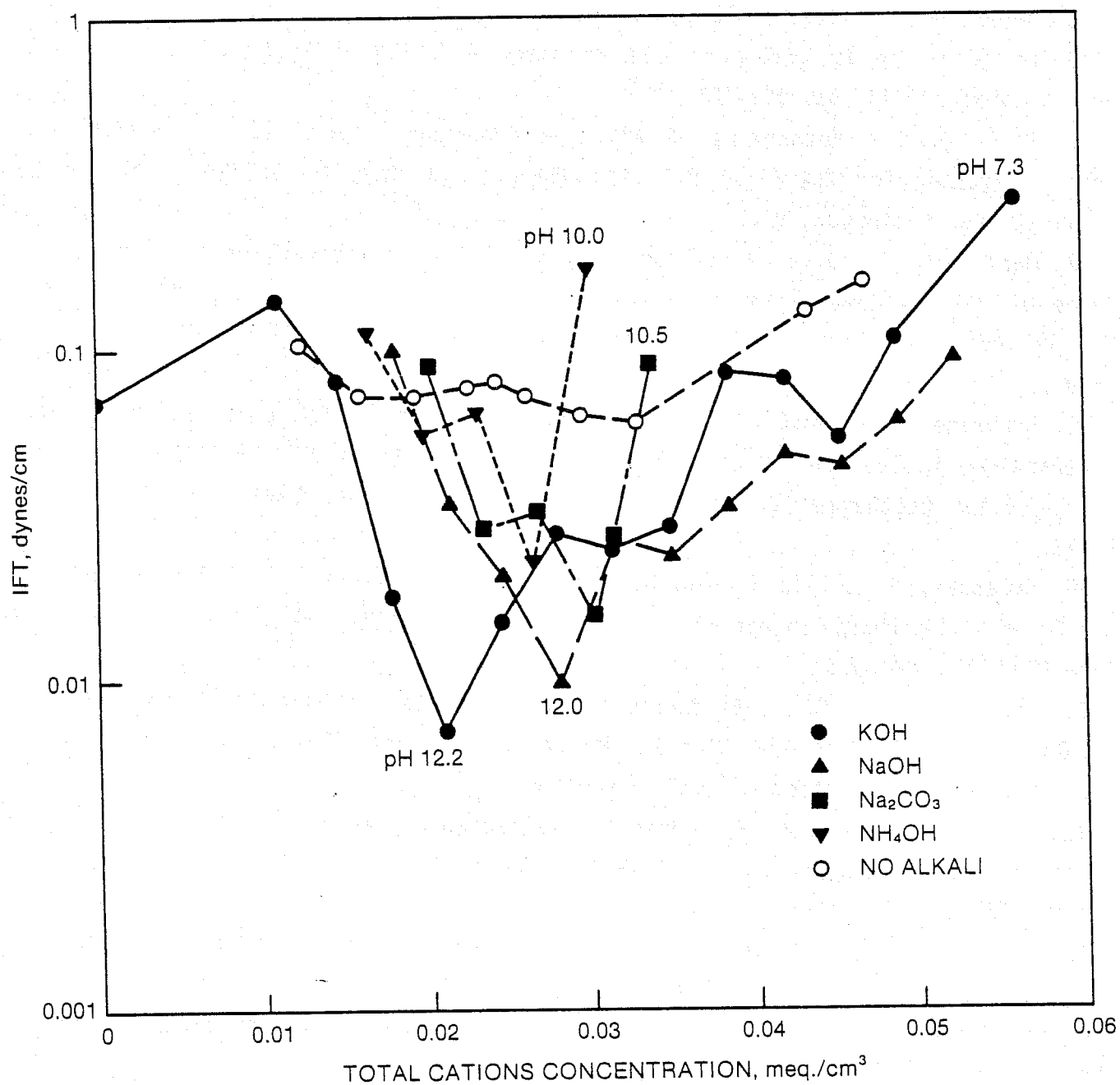


FIGURE 1. - IFT of "J" Sand (Nebraska) oil vs. effective cation content in NaCl brine with 1 % Exxon 914-22 (synthetic sulfonate) and 0.5 % alkali. Figure 8 of reference 27.

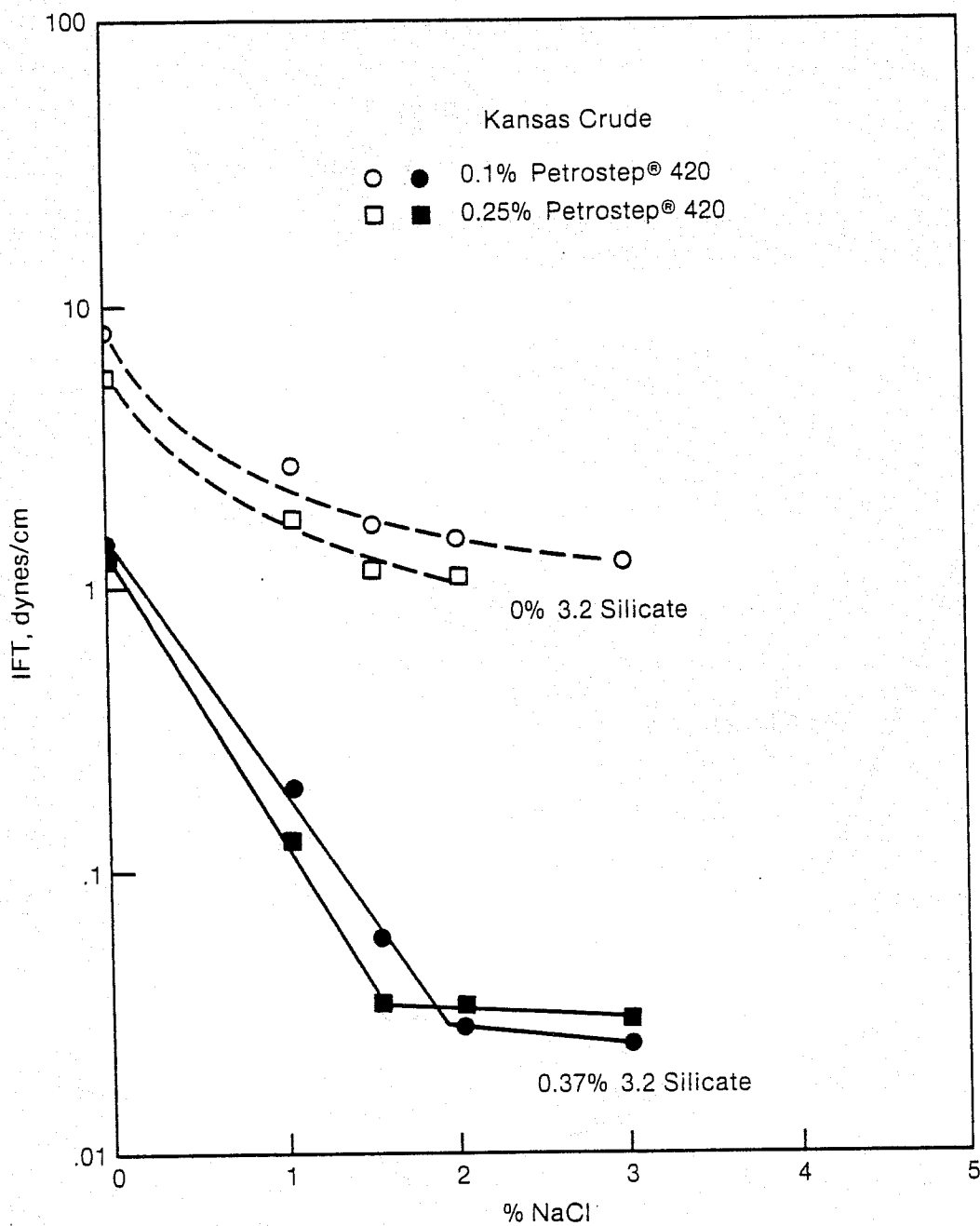


FIGURE 2. - IFT of Kansas crude (acid number 0.19) in brines of various salt and surfactant concentrations, with and without "3.2 silicate" ($\text{SiO}_2/\text{Na}_2\text{O} = 3.2/1$). Figure 1 of reference 19.

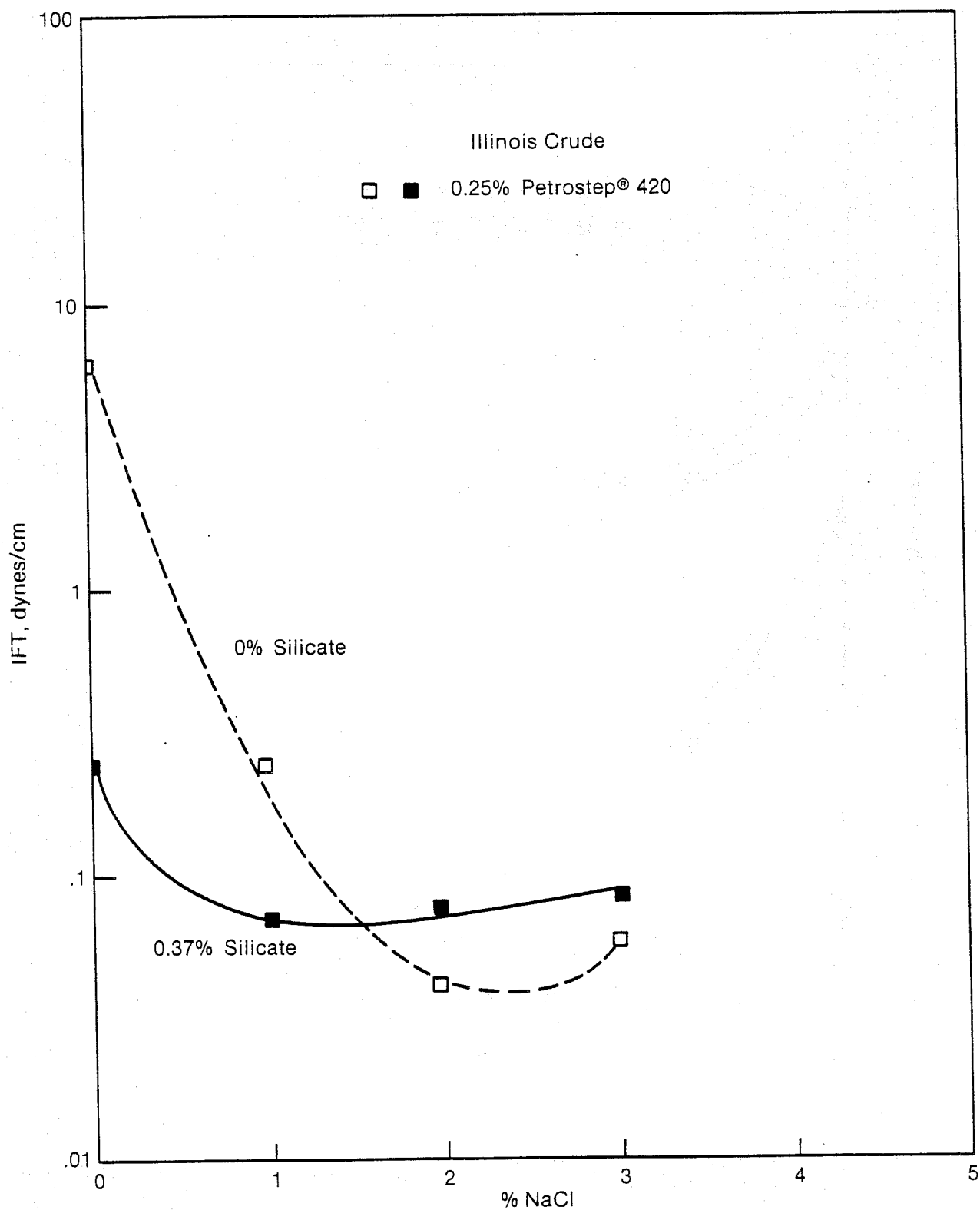


FIGURE 3. - IFT of Illinois crude (acid number 0.10) in surfactant brines of various salt concentrations, with and without 3.2 silicate. Figure 3 of reference 19.

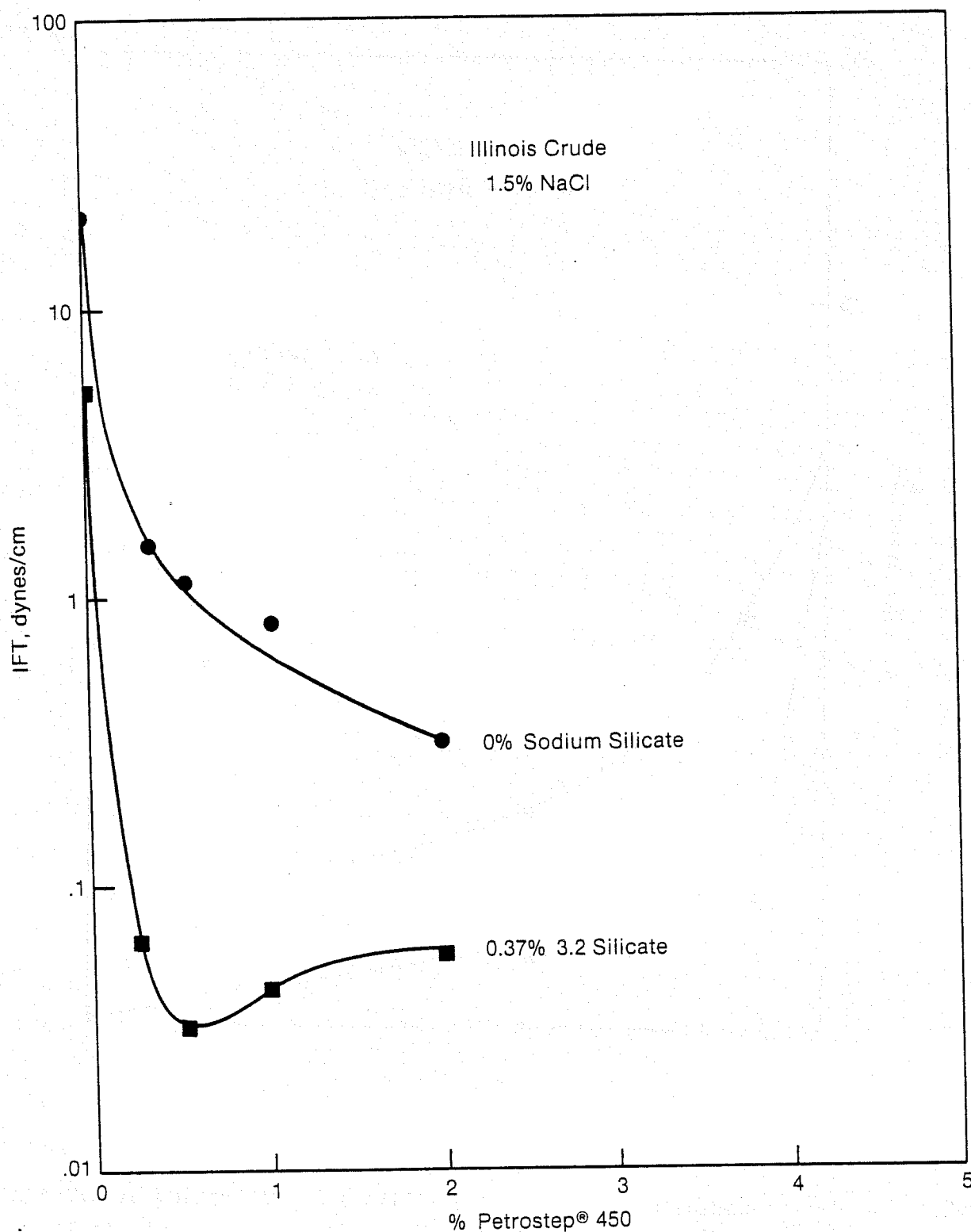


FIGURE 4. - IFT of Illinois crude as a function of surfactant concentration with and without silicate. Figure 4 of reference 19.

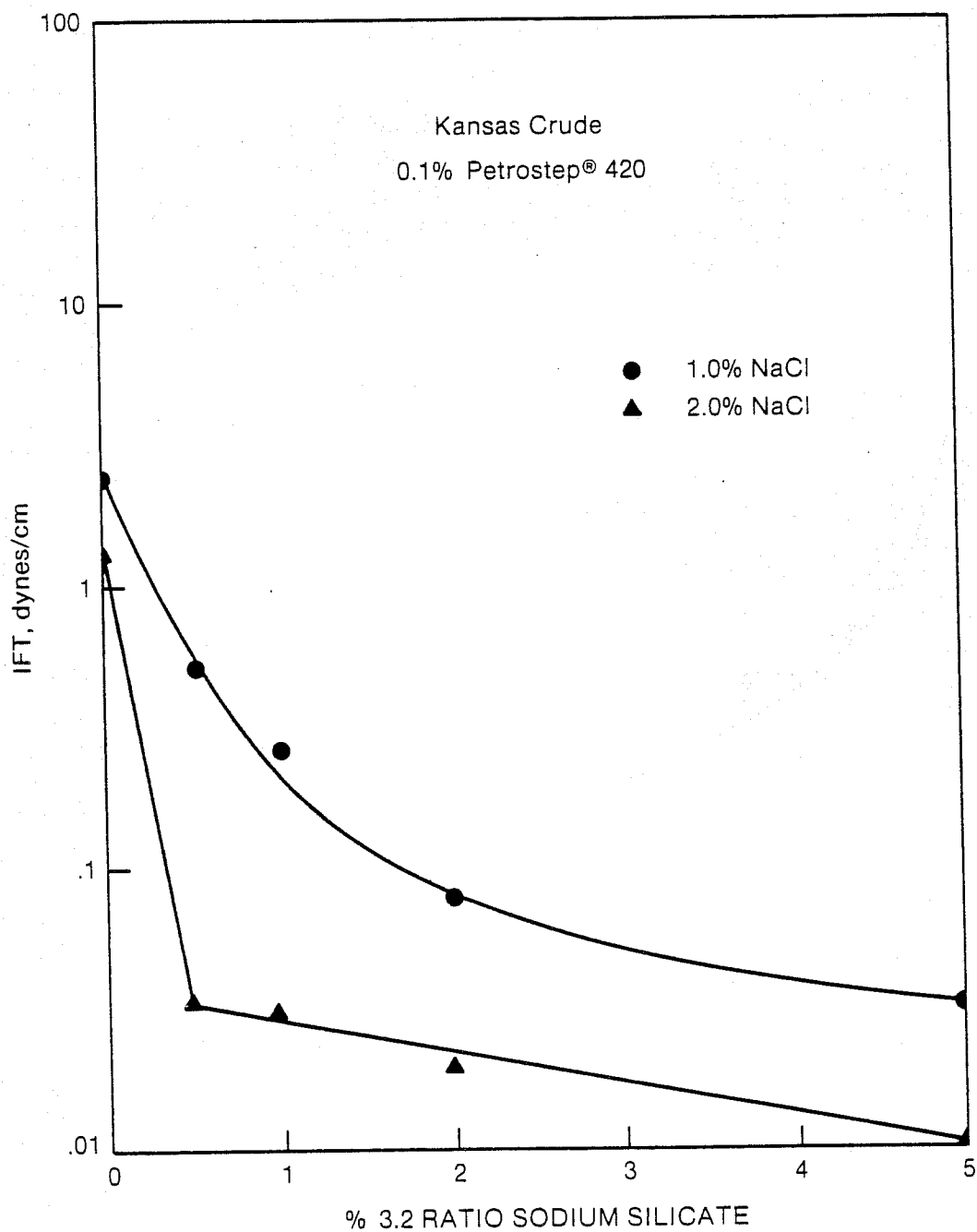


FIGURE 5. - IFT of Kansas crude vs. sodium silicate concentration at two salt levels. Figure 2 of reference 19.

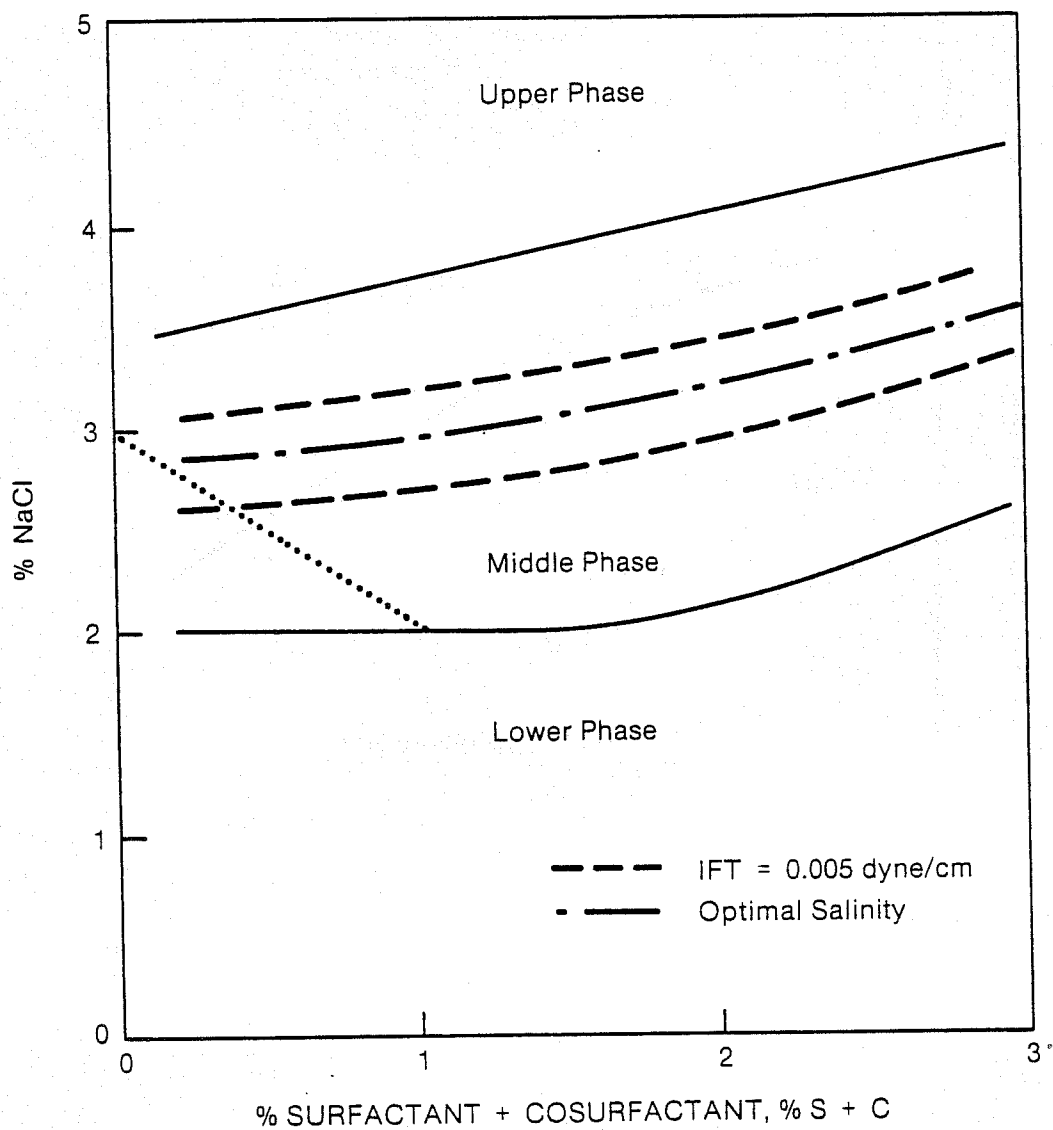


FIGURE 6. - Salinity requirement diagram for an acid oil (acid number 1.4) with a surfactant blend: synthetic sulfonate and ethoxylated alcohol. Figure 3 of reference 18, modified.

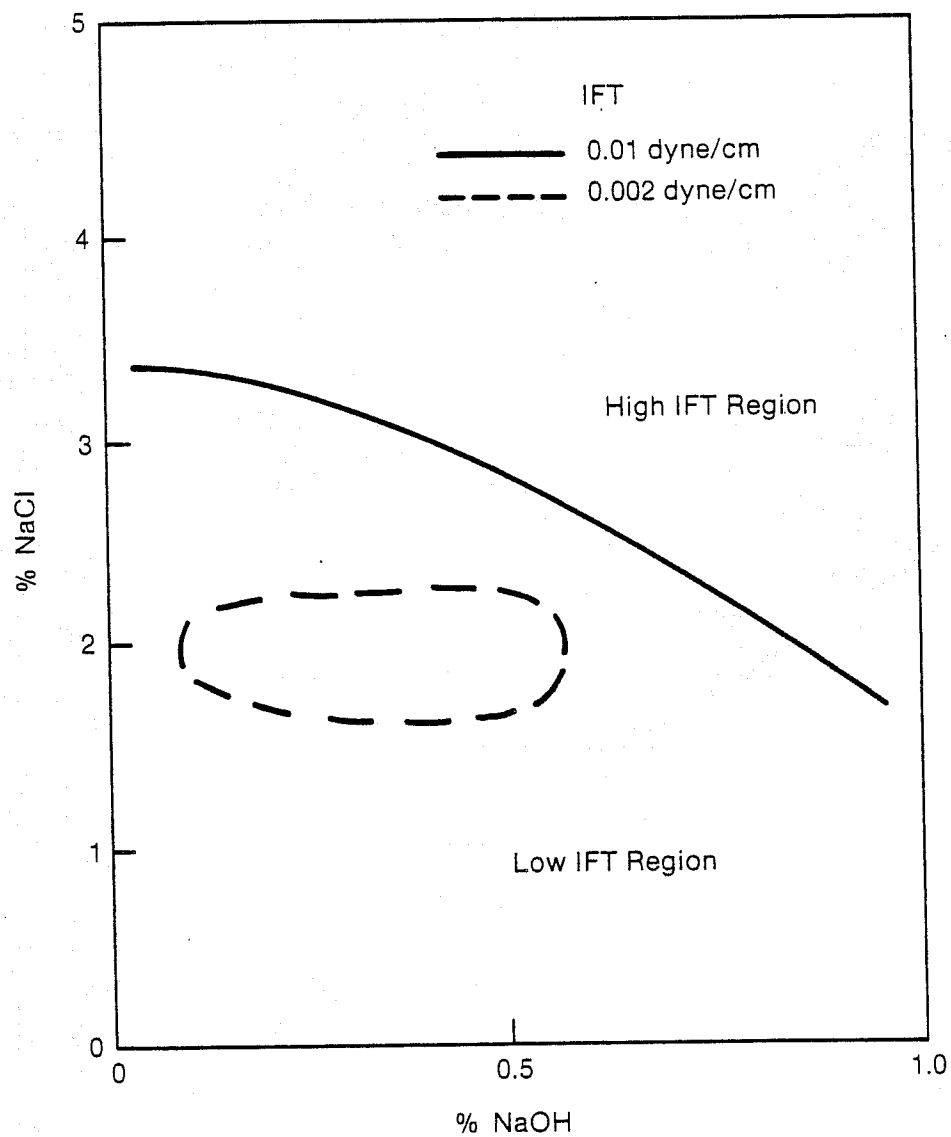


FIGURE 7. - IFT of the oil of figure 6 vs. NaOH and NaCl (2,000 ppm polyacrylamide). Figure 5 of reference 18.

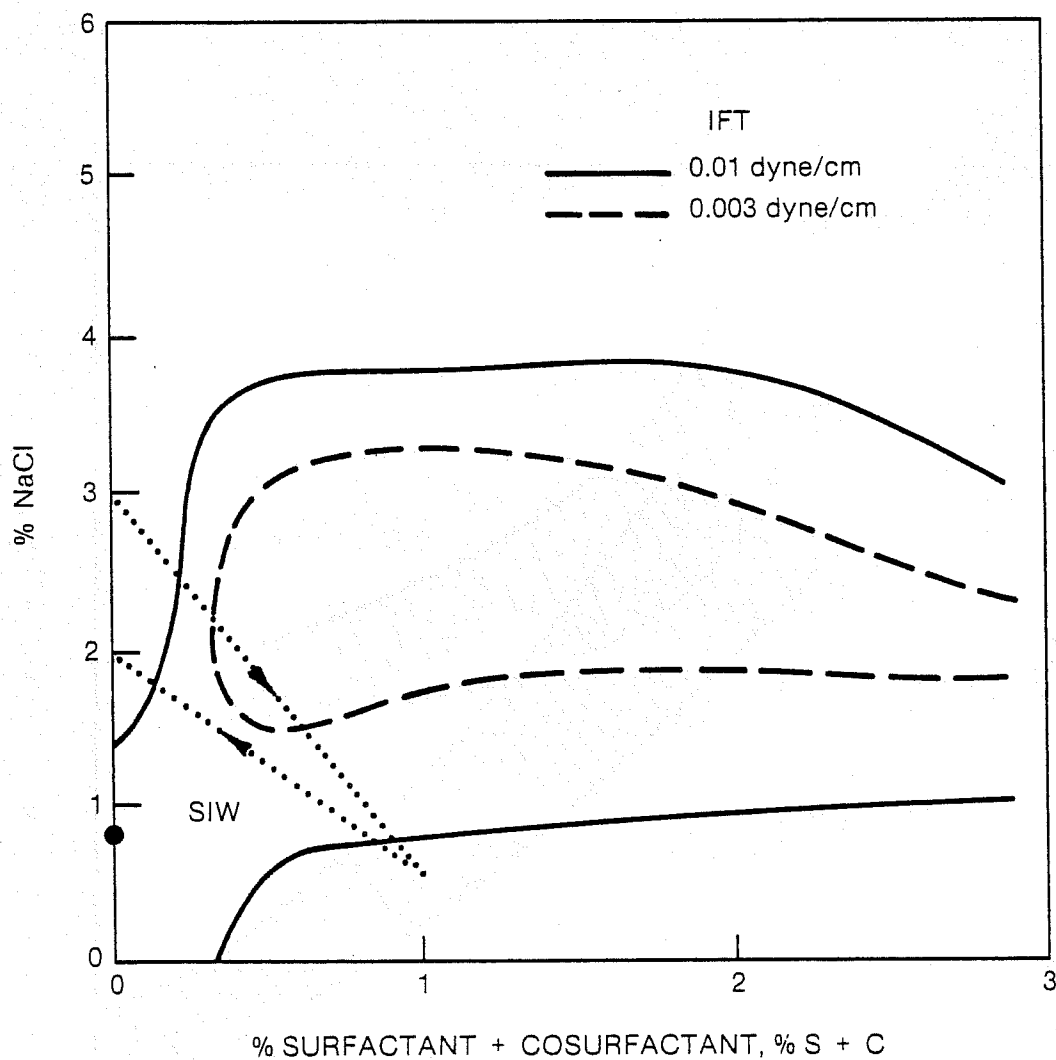


FIGURE 8. - Salinity requirement diagram for oil of figure 6 with 1 % NaOH and 2,000 ppm polyacrylamide. Figure 8 of reference 18, modified.

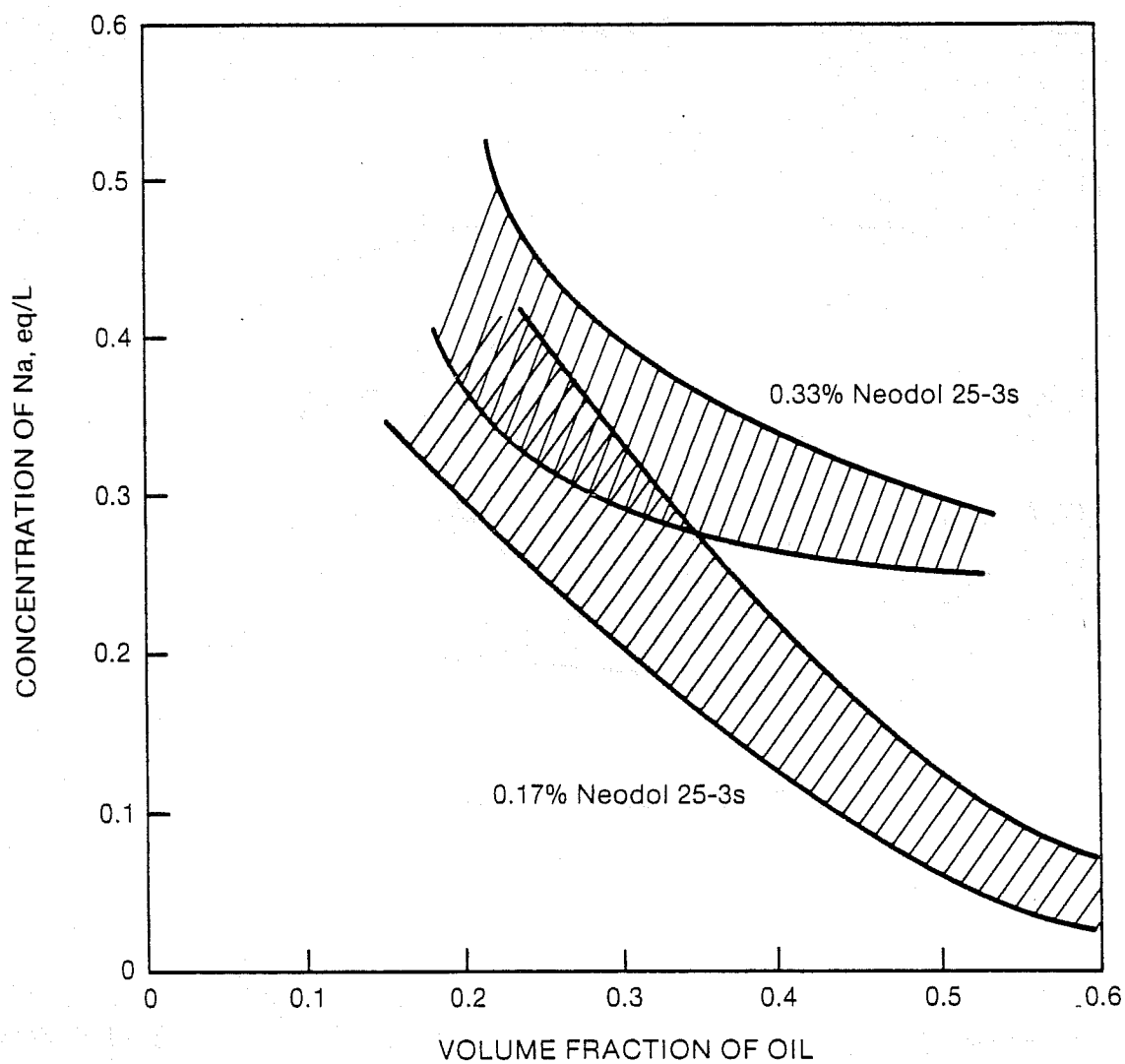


FIGURE 9. - Optimal salinity map for a light (Rocky Mountain) crude oil and silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2/1$). Figure 13 of reference 17.

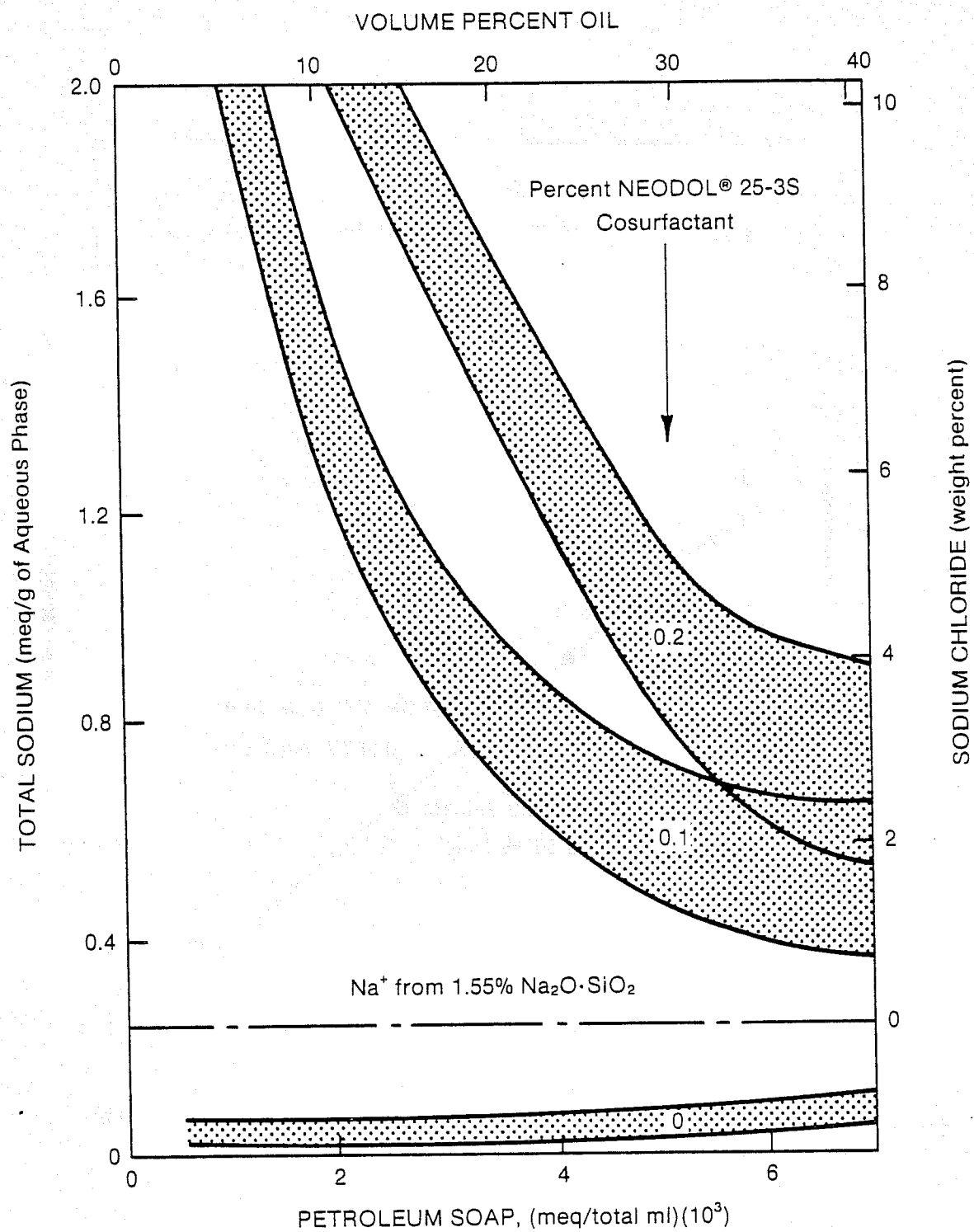


FIGURE 10. - Optimal salinity map for a Gulf Coast crude oil. Figure 1 of reference 6.

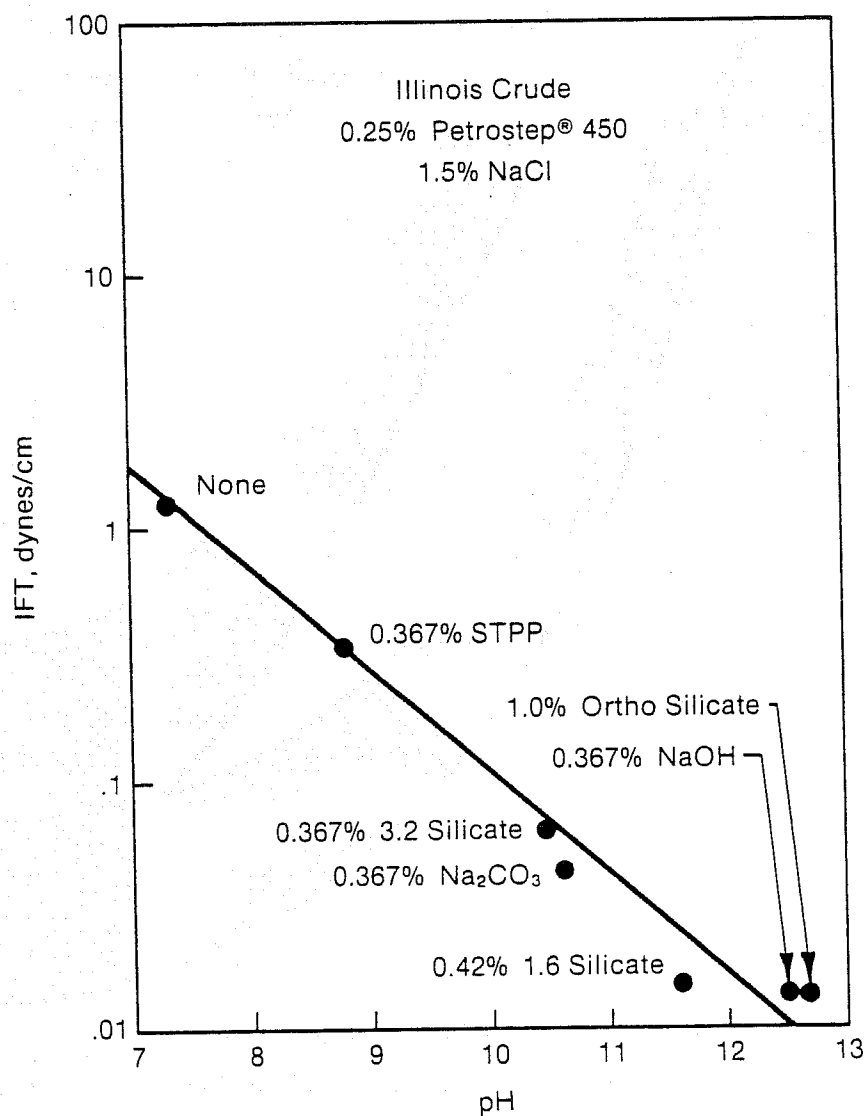


FIGURE 11. - IFT of Illinois crude (acid number 0.10) vs. pH for several alkaline chemicals. Figure 5 of reference 19.

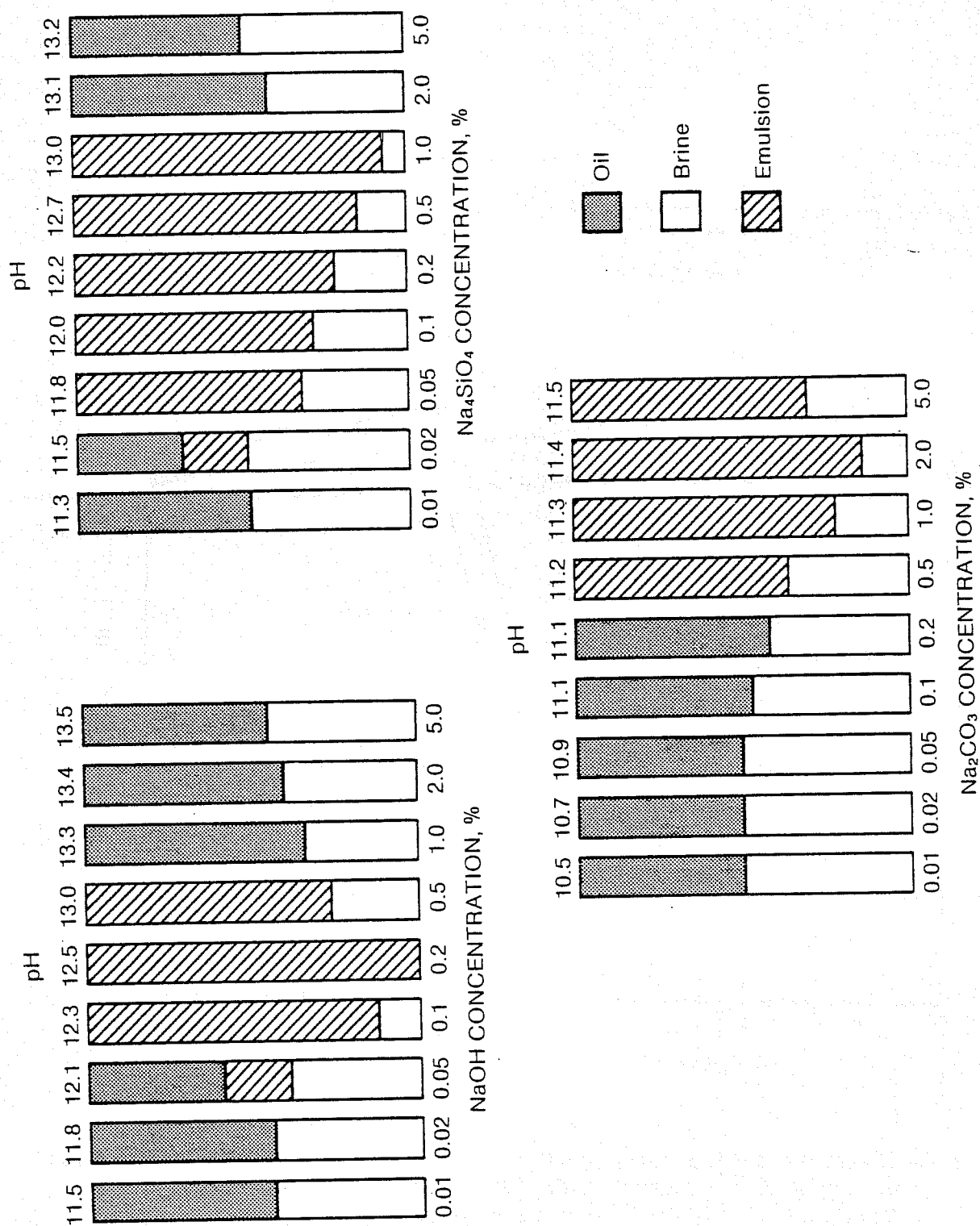


FIGURE 12. - Emulsion phase behavior as a function of alkali concentration for a high-acid crude. Figure 12 of reference 17.

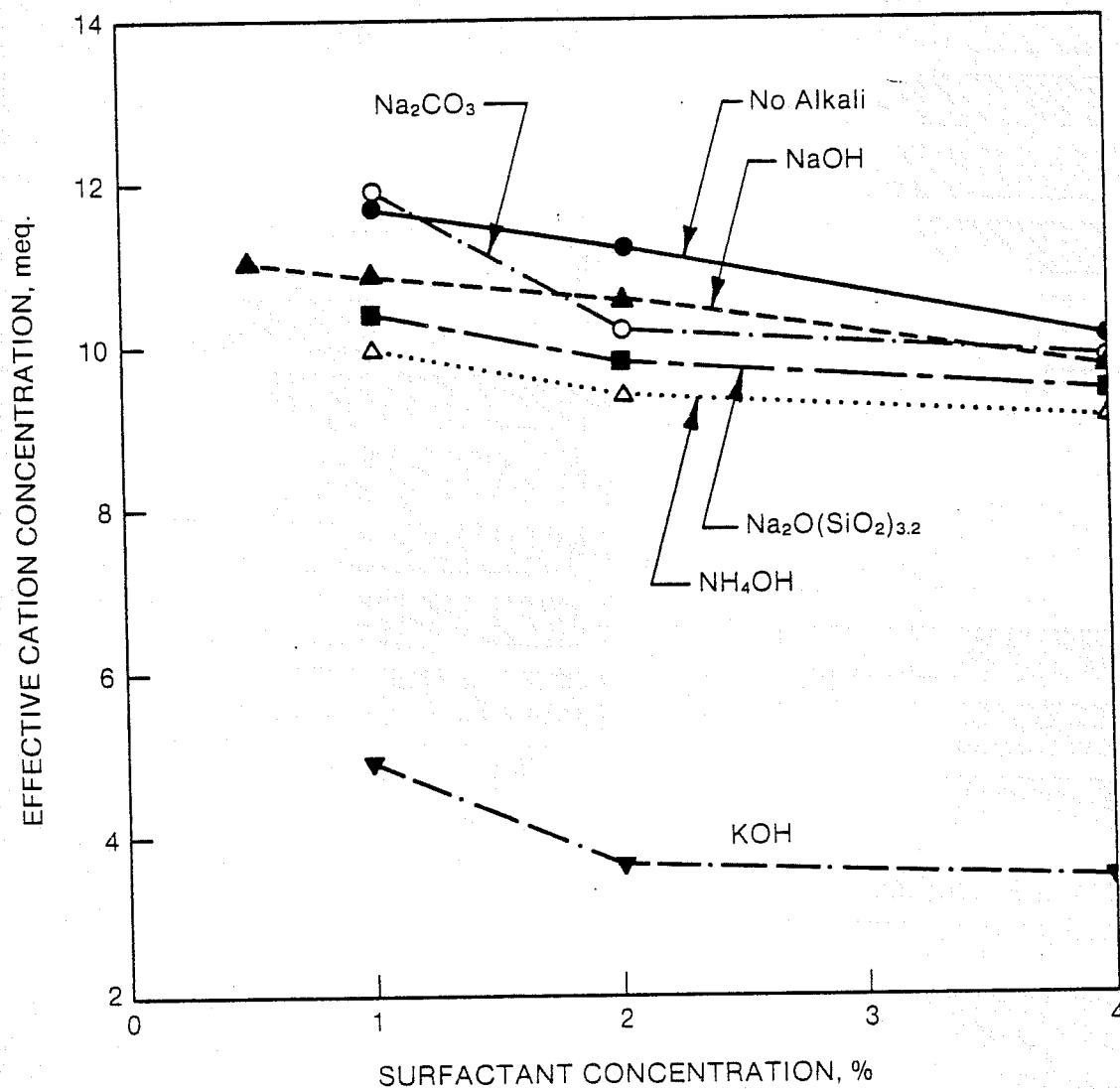


FIGURE 13. - Effective cation concentration at optimal salinity as a function of surfactant concentration (n-tetradecane and 1 % alkaline chemicals). Figure 2 of reference 27.

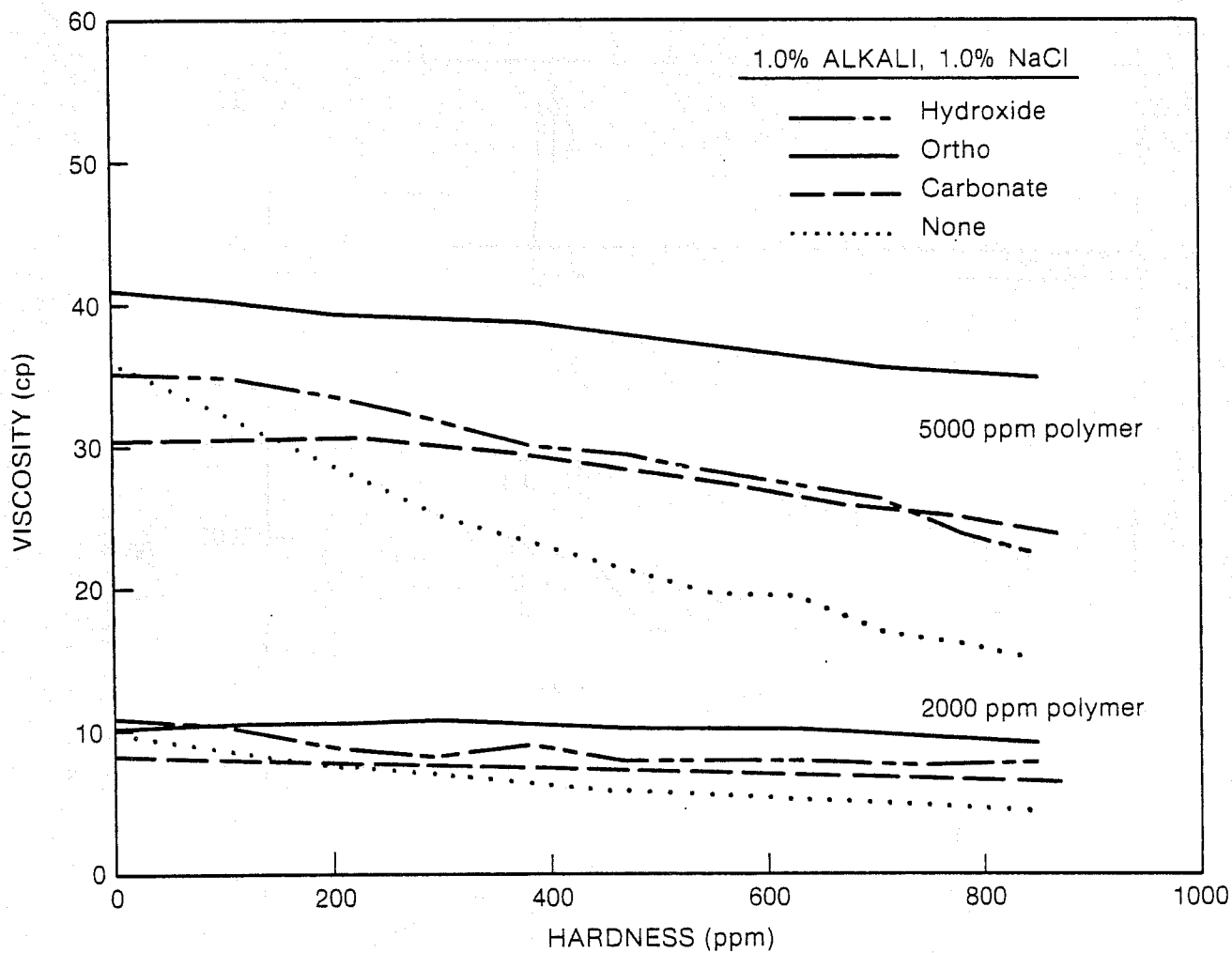


FIGURE 14. - Polyacrylamide viscosity vs. hardness as affected by high alkali levels. Figure 2 of reference 16.

- 1 - Connate Water (4800 ppm Hardness as CaCO_3)
- 2 - Saline Preflush/Postflush
- 3 - Dilute Surfactant Slug

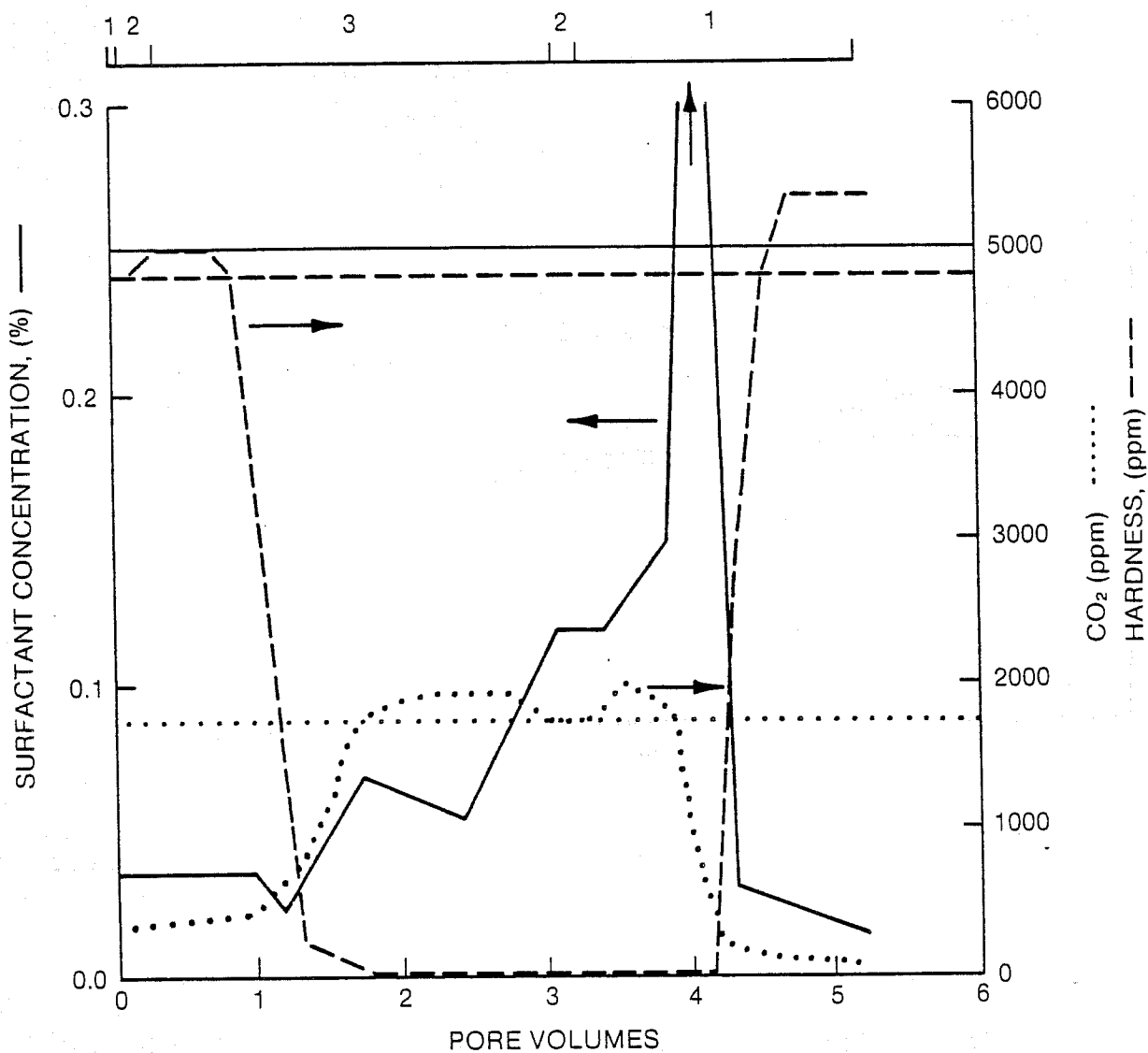


FIGURE 15. - Effluent profiles in a sodium-carbonate-enhanced dilute surfactant flood. Figure 15 of reference 19.

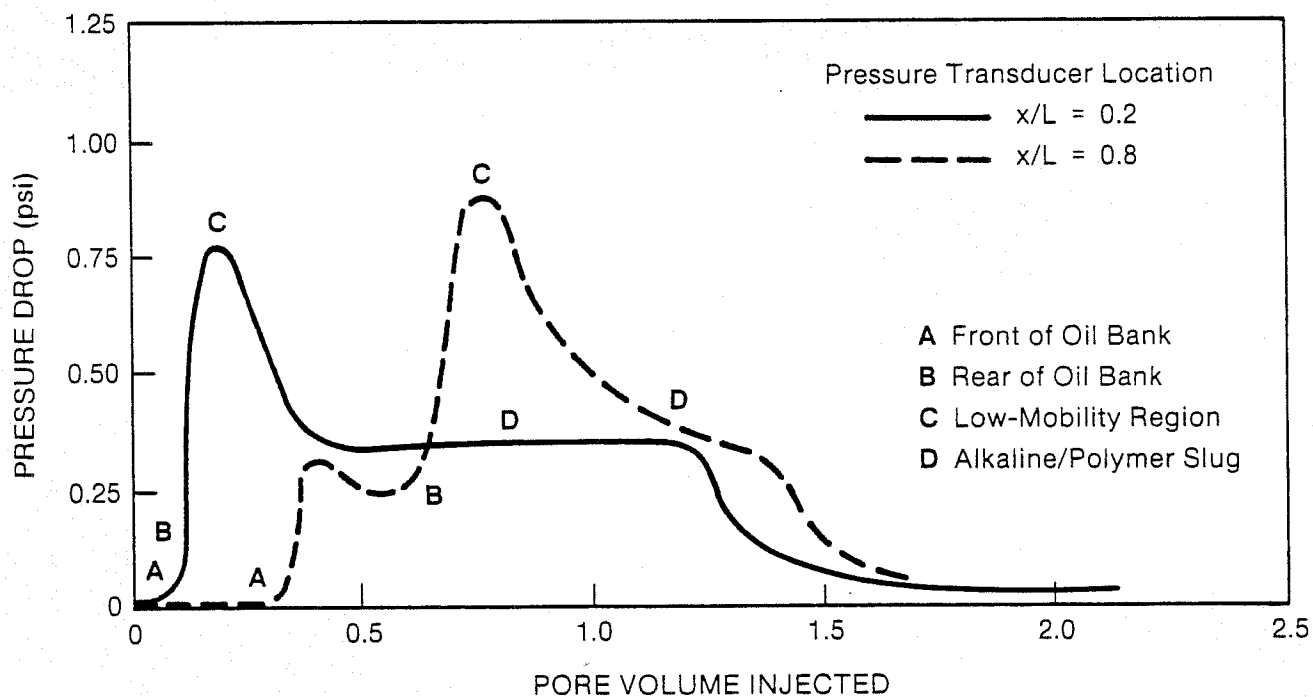


FIGURE 16. - In situ pressure drop for a surfactant-alkaline-polymer flood with an acid oil (acid number 1.4). Figure 12 of reference 18.

